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We have observed the initial oxidation process on Si(001) at 20–700 °C in 10^{-7}–10^{-4} Torr O_2 pressure by high-resolution Rutherford backscattering spectroscopy. The oxygen coverage saturates at 1.45 ± 0.2 ML (1 ML$=6.78\times10^{14}$ cm^{-2}) and 2.3 ± 0.3 ML at room temperature (RT) and 640 °C, respectively. The oxidation of the second layer is found to start before the first layer oxidation is completed even at RT. Further oxidation proceeds basically in the layer-by-layer mode, although there is a compositional transition layer of sub-nm thickness in the interface.

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Reduction of the thickness of gate oxide films in ultralarge-scale-integrated circuits is a crucial issue in shrinking design rules. Metal–oxide–semiconductor field-effect transistor devices with oxide layers of 1.1 nm thickness have already been fabricated in laboratories.[1] For further reduction, the initial oxidation process on Si(001) surfaces should be clarified. A recent study with scanning reflection electron microscopy (SREM) revealed that the oxidation proceeds in the layer-by-layer mode.[2] A barrierless oxidation of the first layer was observed to occur at room temperature (RT), and the energy barrier of the second layer of oxidation was determined to be 0.3 eV. This suggests the possibility of formation of a SiO_2 layer as thin as one monolayer thickness (~0.3 nm). Previous studies, however, reported the existence of transition layers of 0.5–2.5 nm thickness at the SiO_2/Si(001) interface,[3–7] suggesting that the composition and/or structure of such a ultrathin oxide layer of sub-nm thickness is different from thicker oxide layers.

From the theoretical viewpoint, the backbond (BB) site of the down dimmer atom is known to be the most preferable site for oxygen adsorption.[8] Based on first-principles calculations, oxidation of BB sites was shown to be via an apparently barrierless reaction in accordance with the SREM observation.[9] The scanning tunneling microscopy (STM) scanning tunneling spectroscopy observations also suggested that oxygen atoms adsorb on the BB sites in the early stage of oxidation,[10–12] although direct imaging of the adsorbed oxygen atom by STM is rather difficult.[13] After one BB site is oxidized, the first-principles calculation showed that the second layer bonds are energetically preferred to the other Si-Si bonds of the first layer.[14,15] This results in vertical growth rather than layer-by-layer growth in contradiction to the SREM observation. Thus the initial oxidation process is still unclear. Especially, information about the composition and structure of the oxide layer in the initial oxidation stage is not sufficient for full understanding of the oxidation process.

In the present paper, the initial oxidation process on Si(001) is observed by high-resolution Rutherford backscattering spectroscopy (HRBS). HRBS allows us to measure oxygen depth profiles with depth resolution at an atomic level.[16,17] Sequential oxidation by oxygen isotopes was employed to see the dynamics of the initial oxidation process.[6] The results of the HRBS measurement indicate that second layer oxidation starts before the first layer oxidation is completed even at RT.

An ultrahigh vacuum (UHV) scattering chamber (base pressure 8×10^{-11} Torr) was connected to a 4 MV Van de Graaff accelerator via a differential pumping system. A clean Si(001) (2×1) surface was prepared *in situ* by flashing a Si(001) wafer at ~1150 °C. A Si buffer layer of ~100 nm thickness was deposited at 650 °C with an electron beam evaporator to prepare a flat and clean surface. Oxidation of the Si(001) was carried out by introducing molecular oxygen into the scattering chamber. Both $^{16}O_2$ (99.995%) and $^{18}O_2$ (95%) gases were used for sequential isotopic exposures to see the dynamics of the oxidation.[6]

A beam of 350 keV He^+ ions from the accelerator was collimated to 2×2 mm^2 and a divergence angle of less than 1 mrad by a series of apertures. The beam current, which was monitored by a vibrating beam chopper, was ~25 nA, and a typical dose for one HRBS measurement was 15 μC (1.6×10^{15} ions cm^{-2}). The measurement was usually performed on a new area of the sample to avoid radiation damage, although there was no detectable change in the spectrum even if the measurement was repeated on the same position.

The ions scattered at 50 ° from the Si sample were energy analyzed by a 90 ° sector magnetic spectrometer. The acceptance angle of the spectrometer was 0.3 msr. The best energy resolution observed using the present HRBS system was 0.33 keV at 292 keV, including the energy spread of the incident beam. A quadrupole electrostatic lens was installed just before the spectrometer to correct the so-called ''kinematic broadening.''[18] The estimated kinematic broadening without the correction is about 2 keV for 350 keV He ions scattered from ^{16}O atoms under the present experimental conditions. Because the corresponding depth resolution is about 0.5 nm, the correction for the kinematic broadening is essential to achieve atomic level depth resolution.

Figure 1 shows examples of the HRBS spectra observed under [011] channeling conditions. The spectra for the clean surface (closed circles), after 20 min oxidation at RT under $^{16}O_2$ gas pressure of 2×10^{-6} Torr (open circles), and after an additional 20 min oxidation at 640 °C under $^{18}O_2$ gas pressure of 2×10^{-6} Torr (triangles) are shown. These oxi-

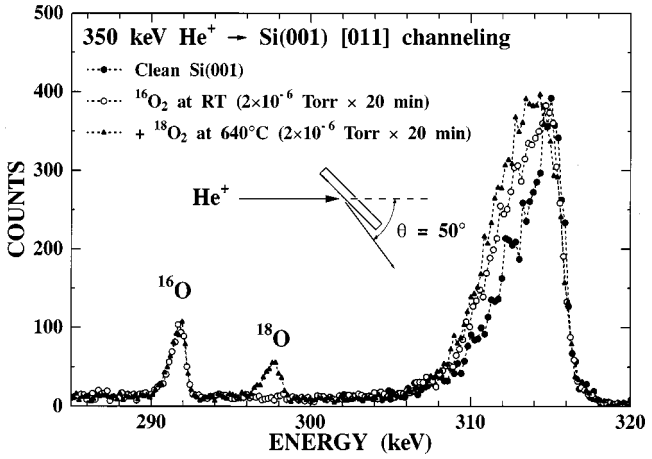

FIG. 1. Observed HRBS spectra for a clean Si(001) surface (closed circles), after 20 min oxidation under $^{16}O_2$ gas pressure of 2×10^{-6} Torr at room temperature (open circles), and after additional 20 min oxidation under $^{18}O_2$ gas pressure of 2×10^{-6} Torr at 640 °C (triangles). The ^{16}O peak is not changed by the additional oxidation at 640 °C.

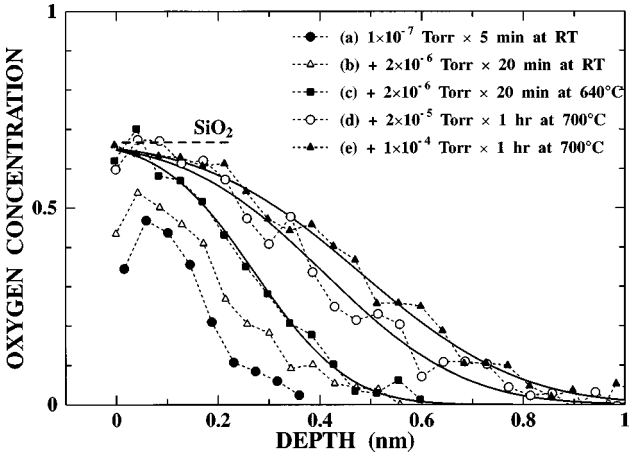

FIG. 2. Oxygen depth profiles observed during the initial oxidation process. Formation of stoichiometric SiO_2 layer is seen after oxidation at 640 °C. The profile moves to deeper region without a significant shape change, indicating the layer-by-layer growth mode.

dation conditions are the same as those in the previous SREM study,[2] where the oxidation of the first (second) layer was observed at RT (640 °C). In the HRBS spectra, separated peaks of ^{16}O and ^{18}O signals are clearly seen at around 292 and 298 keV, respectively.

The amounts of ^{16}O and ^{18}O atoms were derived from the observed HRBS spectra at various oxidation conditions. The oxygen coverage θ was found to be saturated at RT as well as at 640 °C, while no clear saturation was observed at 700 ° in agreement with the previous report.[2] The observed saturation coverage was 1.45 ± 0.2 ML (1 ML$=6.78\times10^{14}$ cm^{-2}) and 2.3 ± 0.3 ML at RT and 640 °C, respectively. These values indicate that the first (second) Si layer is not completely oxidized at RT (640 °C). It should be noted that the ^{16}O yield was not changed by the additional $^{18}O_2$ oxidation at 640 °C (see Fig. 1) showing no exchange of oxygen atoms during oxidation at 640 °C. This is different from the MEIS observation for relatively thicker oxide layers (1.5–5 nm) at higher temperatures (1020–1170 K), where the exchange of oxygen atoms at the surface region during oxidation was reported.[6]

From the observed HRBS spectrum, the oxygen depth profile was derived. Here, we employed a simple procedure, i.e., oxygen concentration was calculated from the yields of oxygen and silicon at the same depth taking account of the cross-section difference. The stopping power of a typical thermal oxide ($\rho=2.35$ g/cm^2) was used in conversion from energy to depth. There might be an error of several percent in the depth scale because the stopping power of the pure Si is larger than that of the typical thermal oxide film by ~8% for ~300 keV He ions.

Figure 2 shows the obtained oxygen depth profiles at various oxidation conditions. After oxygen exposure of 2400 L (Langmuir: 1×10^{-6} Torr s) at RT [profile (b)], the oxygen concentration reaches 50% at the surface region, showing formation of a SiO-like oxide layer. An almost stoichiometric SiO_2 layer is formed by oxidation at 640 °C [profile (c)]. In further oxidation, the oxygen profile moves deeper without a significant change in shape, indicating that the oxidation process is basically layer-by-layer in harmony with the SREM observation.[2]

The observed oxygen profile can be fitted reasonably well by an error function as shown by solid curves in Fig. 2. The standard deviation σ of the error function is 0.28 and 0.32 nm for the profiles (d) and (e), respectively, while the contribution of the instrumental energy resolution ($\delta E\sim0.6$ keV, estimated from the shape of Si leading edge) and the energy loss straggling is much smaller (estimated σ is about 0.12 nm with Lindhard formula[19] and about 0.13 nm with Yang formula[20] including δE). This indicates the existence of a compositional transition layer of $\sigma\sim0.3$ nm[21] in the SiO_2/Si(001) interface in accordance with the recent theoretical studies by Pasquarello *et al.*,[22] and Ng and Vanderbilt.[23] Using first-principles molecular dynamics, they found a transition layer of ~0.5 nm thickness having stoichiometry close to SiO.[22]

Careful analysis of the HRBS spectra observed during the sequential isotopic oxidation allows us to deduce more detailed information. There were several theoretical studies about the initial oxidation process.[9,13–15,24] A scenario for laterally uniform oxidation of the first layer was proposed by Uchiyama *et al.*[15]: After one BB site of each down dimer atom is occupied at $\theta=0.5$ ML, 0.5 ML of oxygen atoms occupy the dimer-bridge (DB) sites, and then the other BB sites of the down dimmer atoms are occupied by 0.5 ML of oxygen atoms at $\theta=1.5$ ML. Demkov and Sankey proposed a ''peeling'' oxidation mechanism, which explains the layer-by-layer oxidation.[24] According to their model, dimer units having four oxygen atoms [one terminal oxygen, one oxygen atom in the DB site and two oxygen atoms in the BB sites] are formed in the first layer oxidation, opening a channel for the second layer oxidation. The tendency for oxygen agglomeration was observed by infrared spectroscopy[25] and also by ultraviolet photoemission spectroscopy.[26] IR absorption spectroscopy revealed formation of surface silicon ep-

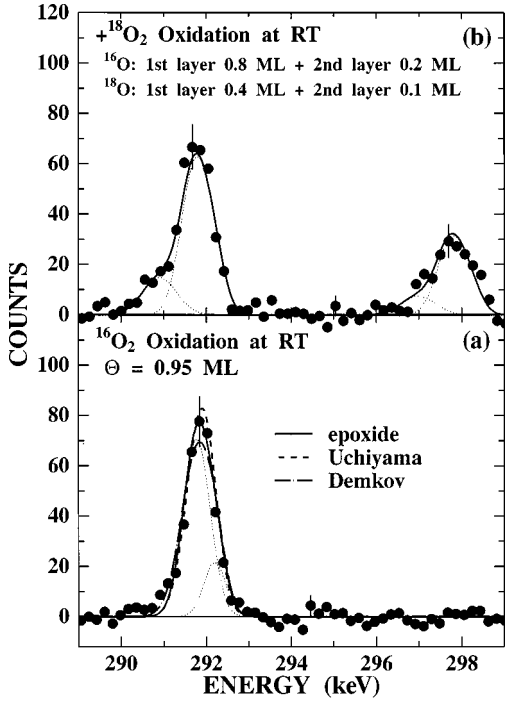

FIG. 3. HRBS spectra observed in sequential isotopic oxidation. Oxidation conditions were (a) 5 min under $^{16}O_2$ gas pressure of 1×10^{-7} Torr at RT; and (b) additional 20 min oxidation under $^{18}O_2$ gas pressure of 2×10^{-6} Torr at RT. Simulated spectra with various oxidation models are shown by curves (a). Typical eror bars are also shown.

oxide structures that contain 3–5 oxygen atoms in single dimer units [one oxygen atom in the on-dimer (OD) site and 2–4 atoms in the BB sites].[25] Based on *ab initio* quantum chemical cluster calculations, the epoxides were found to be the thermodynamically favored product.[25] Observed HRBS spectra are compared with these three models.

Figure 3(a) shows the background subtracted oxygen spectra observed after 5 min oxidation at RT under $^{16}O_2$ gas pressure of 1×10^{-7} Torr. The oxygen coverage is estimated to be 0.95 ± 0.2 ML. The calculated spectra are also shown for comparison. These spectra were calculated as a sum of the contributions from individual sites, which were assumed to be given by Gaussians. For example, dotted curves show the individual contributions for the epoxide model, i.e., the contribution of the OD site (small peak) and that of the BB site [an epoxide structure containing five oxygen atoms, $(O_2)SiØSi(O_2)$, was employed]. The peak energy E_p of the individual contribution was calculated as

$$E_p = K\left(E_0 - \sum_{i=\mathrm{Si,\,O}} \frac{S(i)[N(i)+n(i)/2]}{\cos\theta_i}\right) - \sum_{i=\mathrm{Si,\,O}} \frac{S'(i)[N(i)+n(i)/2]}{\cos\theta_e}, \quad (1)$$

where K is the kinematic factor for He-O scattering, E_0 is the incident energy, $N(i)$ is the area density of i species (i = Si,O) located higher than the relevant oxygen site, $n(i)$ is that located at the same height as the relevant oxygen site,[27] $S(i)$ and $S'(i)$ are the stopping cross sections of i species for He ions before and after scattering, respectively, and $\theta_i(\theta_e)$ is the incident (exit) angle. The peak width was calculated from the instrumental energy resolution ($\delta E\sim0.6$ keV) as well as the energy-loss straggling estimated with the Lindhard formula.[19] The calculated spectra for various oxidation models are almost the same. Although the epoxide model gives a slightly better fit, the results of other models can be improved if the instrumental energy resolution is changed by $\sim10\%$, indicating that a definite judgment on these three models is difficult. It is, however, clear that the oxygen atoms are predominantly incorporated in the first atomic layer at this stage of oxidation (the amount of the second layer oxygen was estimated to be less than 0.1 ML using the fitting procedure described below).

An additional oxidation by $^{18}O_2$ gas was performed at RT (2×10^{-6} Torr, 20 min). Figure 3(b) shows the observed HRBS spectrum. The ^{16}O peak becomes broader and shows a shoulder at $\sim$291 keV while the yield is almost the same as before. This indicates that some ^{16}O atoms move into deeper layers during the additional oxidation.

The observed spectrum was fitted by simulated spectrum taking account of the oxidation of deeper layers. The best-fitted result is shown by a solid curve. The contributions of individual layers are shown by dotted curves. In the simulation, we employed the epoxide model $[(O_2)SiØSi(O_2)]$ for the first layer oxidation and the oxygen atoms incorporated in the second layer were assumed to be at the same height as

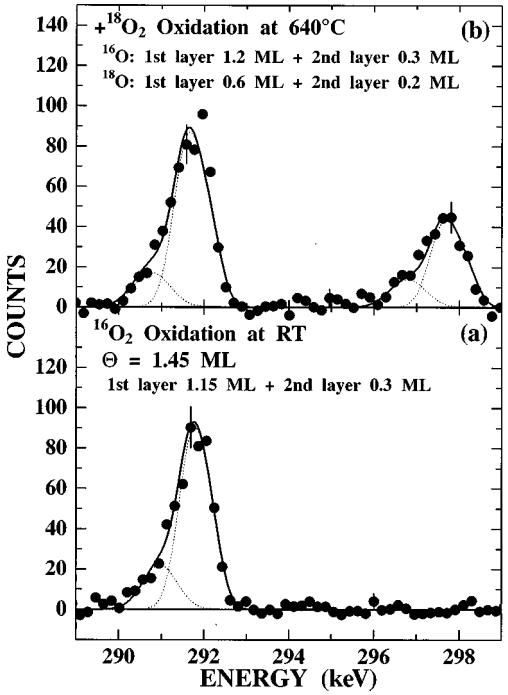

FIG. 4. HRBS spectra observed in sequential isotopic oxidation. Oxidation conditions were (a) 20 min under $^{16}O_2$ gas pressure of 2×10^{-6} Torr at RT; and (b) additional 20 min oxidation under $^{18}O_2$ gas pressure of 2×10^{-6} Torr at 640 °. Simulated best-fitted spectra are also shown by solid curves. The dotted curves show the contributions from individual layers. Typical eror bars are also shown.

the second layer silicon atoms. The amount of $^{16}O(^{18}O)$ atoms in the first layer is found to be 0.8 (0.4) ML and that in the second layer is 0.2 (0.1) ML, showing that 0.1–0.2 ML of ^{16}O atoms move from the first layer into the second layer during the additional oxidation at RT. The present result indicates that most oxygen atoms in the second layer are not directly incorporated at RT. They were incorporated in the first layer before coming to the second layer. The observed second layer oxygen fraction increases very rapidly from $<10\%$ to 20% when the oxygen coverage increases from 0.95 to 1.5 ML. This suggests that surface oxide structures containing more than three oxygen atoms per dimer unit accelerate the second layer oxidation.

Similar measurements were performed at elevated temperatures. Figure 4 shows the result of the sequential oxidation, ^{16}O oxidation at RT (2×10^{-6} Torr, 20 min) followed by ^{18}O oxidation at 640 °C (2×10^{-6} Torr, 20 min). Surprisingly, ^{16}O distribution hardly changes during the additional oxidation at 640 °C in contrast to the sequential oxidation at RT. Newly incorporated ^{18}O atoms distribute in both the first and second layers. The total amount of the first layer oxygen is 1.8 ML, indicating that the first layer is almost completely oxidized at this stage.

In summary, we have observed the initial oxidation process on Si(001) by high-resolution RBS. The coverage of oxygen is found to saturate at 1.45 ± 0.2 and 2.3 ± 0.3 ML at RT and 640 °C, respectively. An almost stoichiometric SiO_2 layer is formed at 640 °C, while a SiO-like layer is formed at RT. Oxygen atoms of $\sim$0.3 ML are incorporated in the second layer before the first layer is completely oxidized even at RT. A part of these second layer oxygen atoms are not directly incorporated but via the first layer. On the contrary, oxygen atoms incorporated at RT does not change their distribution during the additional oxidation at 640 °C. In the further oxidation at elevated temperatures, the oxidation proceeds basically in the layer-by-layer mode although there is a compositional transition layer of subnm thickness in the $SiO_2/Si(001)$ interface.

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[1] G. Timp, in *Proceedings of the 1998 International Electronic Devices Meeting (IEDM)* (IEEE, San Francisco, CA, 1998), Vol. 98, p. 615.
[2] H. Watanabe, K. Kato, T. Uda, K. Fujita, M. Ichikawa, T. Kawamura, and K. Terakura, Phys. Rev. Lett. **80**, 345 (1998).
[3] L. C. Feldman, P. J. Silverman, J. S. Williams, T. E. Jackman, and I. Stensgaard, Phys. Rev. Lett. **41**, 1396 (1978).
[4] A. Ourmazd, D. W. Taylor, J. A. Rantschler, and J. Bauk, Phys. Rev. Lett. **59**, 213 (1987).
[5] H. Akatsu, Y. Sumi, and I. Ohdomari, Phys. Rev. B **44**, 1616 (1991).
[6] E. P. Gusev, H. C. Lu, T. Gustafsson, and E. Garfunkel, Phys. Rev. B **52**, 1759 (1995).
[7] Y. P. Kim, S. K. Choi, H. K. Kim, and D. W. Moon, Appl. Phys. Lett. **71**, 3504 (1997).
[8] T. Uchiyama and M. Tsukada, Phys. Rev. B **53**, 7917 (1996).
[9] K. Kato, T. Uda, and K. Terakura, Phys. Rev. Lett. **80**, 2000 (1998).
[10] P. Kliese, B. Röttger, D. Badt, and H. Neddermeyer, Ultramicroscopy **42-44**, 824 (1992).
[11] Ph. Avouris and D. G. Cahill, Ultramicroscopy **42-44**, 838 (1992).
[12] H. Ikegami, K. Ohmori, H. Ikeda, H. Iwano, S. Zaima, and Y. Yasuda, Jpn. J. Appl. Phys., Part 1 **35**, 1593 (1996).
[13] T. Uchiyama and M. Tsukada, Phys. Rev. B **55**, 9356 (1997).
[14] H. Kageshima and K. Shiraishi, Phys. Rev. Lett. **81**, 5936 (1998).
[15] T. Uchiyama, T. Uda, and K. Terakura, Surf. Sci. **433-435**, 896 (1999).
[16] K. Kimura, K. Ohshima, and M. Mannami, Appl. Phys. Lett. **64**, 2232 (1994).
[17] K. Nakajima, Y. Okazaki, and K. Kimura, Jpn. J. Appl. Phys., Part 1 **39**, 4481 (2000).
[18] H. A. Enge, Rev. Sci. Instrum. **29**, 885 (1958).
[19] J. Lindhard and M. Scharff, K. Dan, Viedensk. Selsk. Mat. Fys. Medd. **28**, 8 (1954).
[20] Q. Yang, D. J. O'Connor, and Z. Wang, Nucl. Instrum. Methods Phys. Res. B **61**, 149 (1991).
[21] Taking account of the possible interface roughness, this is the upper limit.
[22] A. Pasquarello, M. S. Hybertsen, and R. Car, Nature (London) **396**, 58 (1998).
[23] K.-O. Ng and D. Vanderbilt, Phys. Rev. B **59**, 10 132 (1999).
[24] A. A. Demkov and O. F. Sankey, Phys. Rev. Lett. **83**, 2038 (1999).
[25] B. B. Stefanov and K. Raghavachari, Surf. Sci. **389**, L1159 (1997).
[26] H. W. Yeom, H. Hamamatsu, T. Ohta, and R. I. G. Uhrberg, Phys. Rev. B **59**, R10 413 (1999).
[27] The heights of oxygen sites were taken from Fig. 1 of Ref. 24, Fig. 2 of Ref. 25, and private communication with Dr. Uchiyama.